

IONIC CONDUCTIVITY IN GLASSES AND MELTS (UP TO 1650 °C). APPLICATION TO THE CaO-SiO₂ SYSTEM¹

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ABSTRACT

In order to reach electrical conductivity data in oxides, from room temperature up to 1650°C, we built an original setup based on the four-electrode method. This setup has been successfully applied to study the ionic mobility in the alkaline-earth silicate system CaO-SiO₂ from solid state to molten state. Below the glass transition temperature T_g, the transport mechanism is thermally activated with a high activation energy value. In the molten state, the deformation of the network enhances the diffusion of the Ca²⁺ cations and the conductivity is well described by the phenomenological Vogel-Tammann-Fulcher (VTF) law.

1. INTRODUCTION

While the electrical conductivity of solid glasses has been extensively studied, only few works were devoted to the charge transport in glass-forming melts at high temperature. The most common method takes advantage of an alumina tube, the extremities of which are painted with platinum and used as electrodes [1]. This type of cell, although simple in its principal, has a major drawback because alumina may interact with liquid oxides and then changes their composition. To avoid this contamination, some authors use a platinum crucible and insert two platinum wires (electrodes) in the melt [2,3]. The geometric factor of the cell is then obtained by a calibration with a standard ionic solution the conductivity of which is well known. However, in the two-electrode method, the data are generally influenced by the polarization effects due to the charge accumulation near the electrodes [4]. In order to reach accurate data in the molten state we built an original device able to perform conductivity measurements at high temperature (up to 1650 °C) over a wide frequency range (1Hz-1MHz). This device has been applied to study the transport mechanism in the molten and undercooled states of the alkaline-earth silicate system CaO-SiO₂. Furthermore, a calibration-free technique

has been used in order to complete the conductivity measurements in the solid state from 500 °C to 950°C. Even though most of the fast ionic conductors having potential applications in electrochemical devices such as batteries, the conductivity of alkaline earth silicate is non negligible and the role of the migrating calcium cations remains still unclear.

2. EXPERIMENTAL

2.1. Sample preparation

Two compositions in the $x\text{CaO}-(1-x)\text{SiO}_2$ system with $x = 44$ and $x = 50$ mol% were prepared by mixing pre-dried SiO_2 (99.99%) and CaCO_3 (99.95%) powders in the correct proportions. For each sample, the mixture was melted in a Pt crucible at 1650 °C for two hours, and quenched by placing the bottom of the crucible in water. The glass was transparent and free of crystallization as confirmed by the absence of Bragg peaks in XRD spectra. The glass transition temperature T_g (table I) was determined by differential scanning calorimetry (DSC) at a heating rate of 10°C/min. The values of T_g are in good agreement with those reported by Shelby [5] using the dilatometric technique.

2.2. Solid-state measurements

In the glassy state, the electrical conductivity was measured in the temperature range 500°C – 950°C and in the frequency range 100 Hz - 10 MHz using a HP4194A impedance spectrometer and a LabView program for data acquisition. The samples were 0.5 cm² glass pellets with a thickness about 1 mm. Platinum was evaporated as electrodes on both faces of the pellet. The temperature was measured by a Pt/Pt-10%Rh thermocouple located at about 1 mm from the sample.

2.3. Molten-state measurements

An original device for electrical conductivity measurements in the molten state was developed in our laboratory to reach conductivity data up to 1650°C over a wide frequency domain. This set-up is based on the four-electrode method in order to reduce the polarization effects usually observed in the two-point classical method, particularly at high temperature and low frequencies. The cell details are shown in Fig. 1. Further details about the experimental setup, calibration and corrections are given elsewhere [6,7]. The melt is contained in a Pt crucible placed in the middle of a vertical tubular furnace. The electrode system consists of two Pt wires (2 and 3) for voltage drop (U) measurement and two Pt sheets (1 and 4) for current (I) measurement. The electrodes are mechanically linked to a micrometer displacement system, which allows the depth determination with a good precision. The complex impedance of the melt is measured in the frequency range 100 Hz – 1 MHz with the same impedance spectrometer as in the

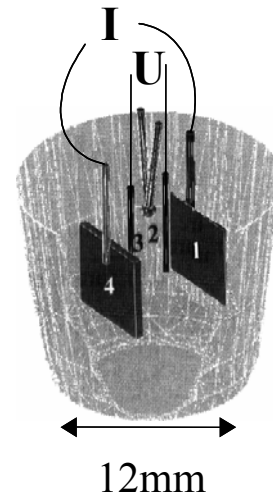


Fig. 1. Platinum crucible and electrode assembly: (1) and (4), current electrodes, (2) and (3) voltage electrodes.

solid state. The measurement of temperature is performed with a Pt/Pt-10%Rh thermocouple, which is located 2 mm above the melt surface. A KCl 1M ionic solution, the conductivity of which is well known [8], is used for the cell calibration at room temperature.

3. RESULTS

3.1. Solid state

The complex electrical conductivity was measured in the two glasses upon heating from 500 °C to 950 °C by step of 20 °C in the frequency range 100 Hz – 10 MHz. The high temperature part is restricted to 950°C because of the softening and the crystallization of the sample. A typical experimental curve is reported in figure 2 in the case of the 0.50CaO-0.50SiO₂ glass. All data have been successfully fitted using the Universal Dielectric Response (UDR) law [9]:

$$\sigma(\omega) = \sigma_{dc} + a\omega^s$$

where $\sigma_{dc} = \sigma(0)$ is the static conductivity, ω the frequency and a and s are phenomenological parameters (with $0 < s < 1$).

The evolution of $\sigma_{dc} \cdot T$ product as a function of the temperature in Arrhenius coordinates is given in figure 3 for the same sample. The curve exhibits a clear crossover occurring at T_g . Below T_g , the $\sigma_{dc} \cdot T$ product follows a straight-line characteristic of a thermally activated transport:

$$\sigma_{dc} \cdot T = A \exp\left(-\frac{E}{kT}\right)$$

where E is the activation energy, A the pre-exponential factor and k the Boltzmann constant. In table I are listed the value of the activation energy as well as the value of the pre-factor A for the two studied glasses.

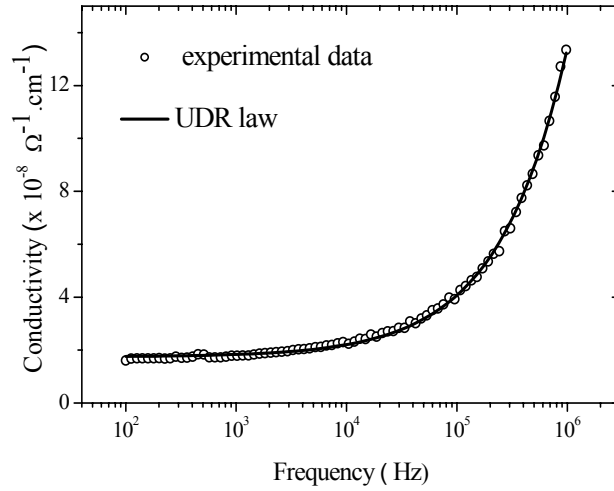


Fig. 2. Frequency dependence of the electrical conductivity at 590°C for the 0.50CaO-0.50SiO₂ glass. Circles are the experimental points, the solid line is the best fit of the experimental data with the UDR law.

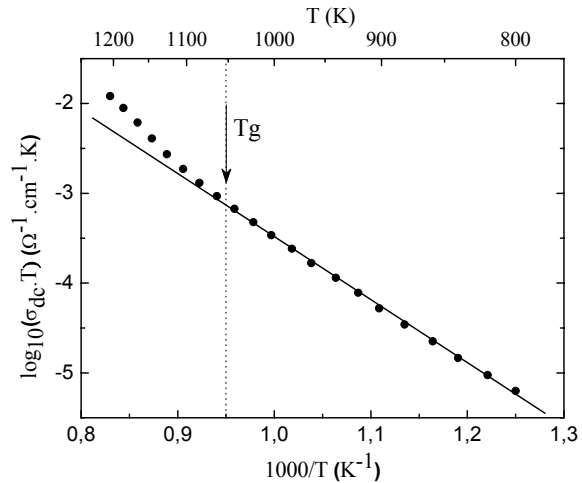


Fig. 3. Temperature dependence of the $\sigma_{dc} \cdot T$ product for the 0.50CaO-0.50SiO₂ glass.

Composition	0.50CaO-0.50SiO ₂	0.44CaO-0.56SiO ₂
T _g (°C)	770	780
E (eV)	1.38	1.42
A (Ω ⁻¹ .cm ⁻¹ K)	3300	1940
Δ (eV)	0.24	0.24
T ₀ (K)	753	780

Table I. Glass transition temperature T_g, Arrhenius and VTF parameters of the xCaO - (1-x)SiO₂ system in solid and molten states.

3.2. Molten state

The solid-state measurements show the onset of a non-Arrhenius conductivity regime above the glass transition temperature. To complete the data above T_g and in the molten state, we used our specific 4-electrode setup. For each sample, the conductivity measurements were performed during a cycle from 1650 °C down to 900 °C with a cooling rate of 150 °C per hour, then on heating the sample up to 1650°C. The conductivity data obtained during this cycle are plotted into the figure 4 for x = 44 and x = 50 melts. We can see an important hysteresis loop in the case of the 0.50CaO-0.50SiO₂ sample. Moreover, a large undercooling interval (190 °C) is observed at this slow cooling rate followed by the onset of crystallisation at 1327 °C, where the conductivity decreases suddenly by more than one decade. Upon heating, the conductivity increases strongly just below the melting temperature (T_m = 1817 K) then reaches the previous values (on cooling) in the molten state. The cycle corresponding to the 0.44CaO-0.56SiO₂ sample is very slim compared to the 0.5CaO-0.5SiO₂ one. This behaviour reveals the relative tendency for the 0.44CaO-0.56SiO₂ melt to vitrify even at a slow cooling rate.

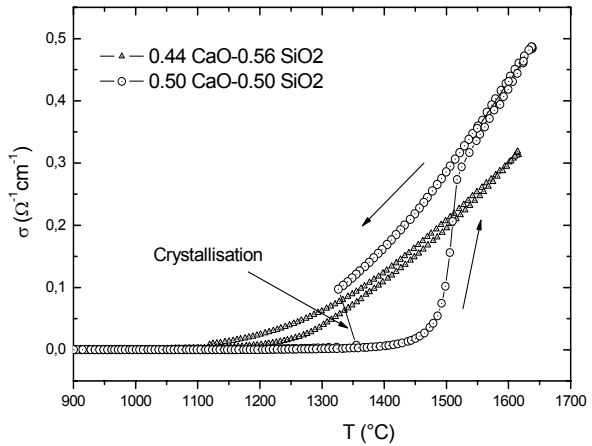


Fig. 4. Electrical conductivity data during a temperature cycle obtained with the molten state setup.

We consider now the conductivity dependence versus temperature only in the liquid and undercooled states. In this temperature range, we were not able to fit the conductivity data with a simple Arrhenius law, but we obtained an excellent fit using the phenomenological Vogel-Tammann-Fulcher (VTF) law:

$$\sigma.T = B \exp\left[-\frac{\Delta}{k(T - T_0)}\right]$$

where B and Δ are constant, T is the absolute temperature and T_0 a temperature called the ideal glass transition. The VTF fit parameters are listed in table I for each sample.

4. DISCUSSION

The use of the solid state setup and the original molten state setup allowed us to measure electrical conductivity of the CaO-SiO₂ system in a wide temperature range (500 to 1650 °C). We followed the conductivity behaviour in several states of this system: liquid, undercooled-liquid and glass. Figure 5 summarizes the obtained data in the case of the 0.5CaO-0.5SiO₂ system (see also table 1).

Some authors suggested that in the absence of alkali cations, it should be very difficult to observe the motion of divalent cations below T_g [10]. Our results, however, show a non-negligible conductivity in the pure alkaline-earth silicate glass even at low temperatures. In the studied glass, each Ca²⁺ cation creates two non-bridging oxygens (NBO) and the ionic conductivity is ensured by the diffusion of the alkaline earth cations along these NBO. Below the glass transition temperature T_g , the electrical conductivity follows an Arrhenius behaviour (Fig. 5) which is characteristic of a thermally activated transport. The activation energy values (table I) found in this study are in agreement with those reported by Gruener et al. in the ternary system CaO-SiO₂-Al₂O₃ with a small amount of alumina [11]. But they are twice as large as the typical values of the alkali silicate glasses [12]. One can expect that the divalent character of the Ca²⁺ cations results in a large binding energy of these cations to non-bridging oxygens.

In the molten state, the conductivity rises faster than the Arrhenius law because of the softening of the network, which enhances the diffusion of mobile species. The transport mechanism becomes cooperative and the conductivity is well described by the VTF law (Fig. 5) which is commonly used to describe the temperature dependence of viscosity for fragile silicate melts [13]. This phenomenological law can be deduced using the free volume theory [14]. The model developed recently by Souquet et al. [15] gives a more precise image to explain the VTF behaviour from the conductivity in alkali silicate melts. After this model, the enhancement of the conductivity results of the local deformations of the macromolecular chains or network above T_g . These deformations, which need local fluctuations of free volume, facilitate the jump of cations along the NBO.

As in the solid state, the electrical conductivity of the CaO-SiO₂ melt is small compared to the alkali silicate melt at a given temperature. The difference can be attributed to the high value of the pseudo-activation energy Δ term (table I). For example, in the K₂O-2SiO₂ melt Δ is about 0.1 eV after the study carried out by Caillot et al. [16].

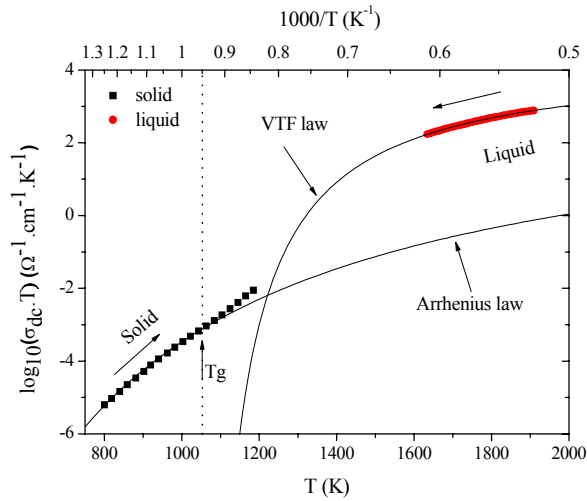


Fig. 5. The whole temperature dependence of the electrical conductivity of the 0.50CaO-0.50SiO₂ system showing the two types of behaviour in the solid and the molten states. The solid lines are the best fits with Arrhenius VTF laws, respectively.

The analysis of table 1 shows the increase of the conductivity with Ca content in the solid state as well as in the molten state. However, in order to study the exact influence of the Ca concentration on the conductivity, more compositions are needed.

CONCLUSION

The electrical properties of the CaO-SiO₂ system have been investigated in a wide temperature range using a specific device we developed in our laboratory. Conductivity data were given in the liquid, undercooled-liquid and glass for two different compositions. In the solid state, the conductivity is ensured by the jump of Ca²⁺ cations along the non-bridging oxygens. This mechanism is thermally activated with a high activation energy value. A second regime was observed in the molten state where the conductivity follows the phenomenological Vogel-Tammann-Fulcher (VTF) law. In this regime, the conductivity is enhanced because the softening and the deformation of the network facilitate the migration of the alkaline-earth cations.

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